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A Systematic Approach for Selecting the Appropriate SPME Fiber

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Overview of Presentation

- Factors that affect fiber selection
- Description of various types of fibers
- Extraction of low-molecular-weight analytes by various SPME fibers
- Extraction of semi-volatile analytes by various SPME fibers
- The effects of analyte size on SPME fibers
- Capacity of SPME fibers

Factors Affecting Fiber Selection

- Analyte molecular weight and shape
- Analyte polarity and functionality
- Minimum detection limits
- Linear range requirements
- Fiber polarity
- Fiber extraction mechanism

Adsorbent vs. Absorbent Fibers

Adsorbent type fibers

- Physically traps or chemically reacts bonds with analytes
  - porous material
  - high surface area
- Analytes may compete for sites
- Fibers have limited capacity

Absorbent type fibers

- Analytes are extracted by partitioning
  - liquid phase
  - retains by thickness of coating
- Analytes do not compete for sites
- Fibers can have high capacity

Types of SPME Fibers

Bare Fused Silica	Adsorbent	Unknown
7µm Polydimethylsiloxane (PDMS)	Absorbent	Nonpolar
30µm PDMS	Absorbent	Nonpolar
100µm PDMS	Absorbent	Nonpolar
85µm Polyacrylate (PA)	Absorbent	Polar
65µm PDMS-DVB, StableFlex™	Adsorbent	Bipolar
65µm CW-DVB, StableFlex	Adsorbent	Polar
85µm Carboxen-PDMS, StableFlex	Adsorbent	Bipolar
55µm/30µm DVB/Carboxen™-PDMS, StableFlex	Adsorbent	Bipolar

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Physical Properties of Divinylbenzene and Carboxen-1006

Material	Surface Area (m^2/g)	Porosity (mL/g)* macro	meso	micro	Total
Divinylbenzene	750	0.58	0.85	0.11	1.54
Carboxen™ 1006	720	0.23	0.26	0.29	0.78

*Macropore = >500Å, Mesopore = 20-500Å, Micropore = 2-20Å

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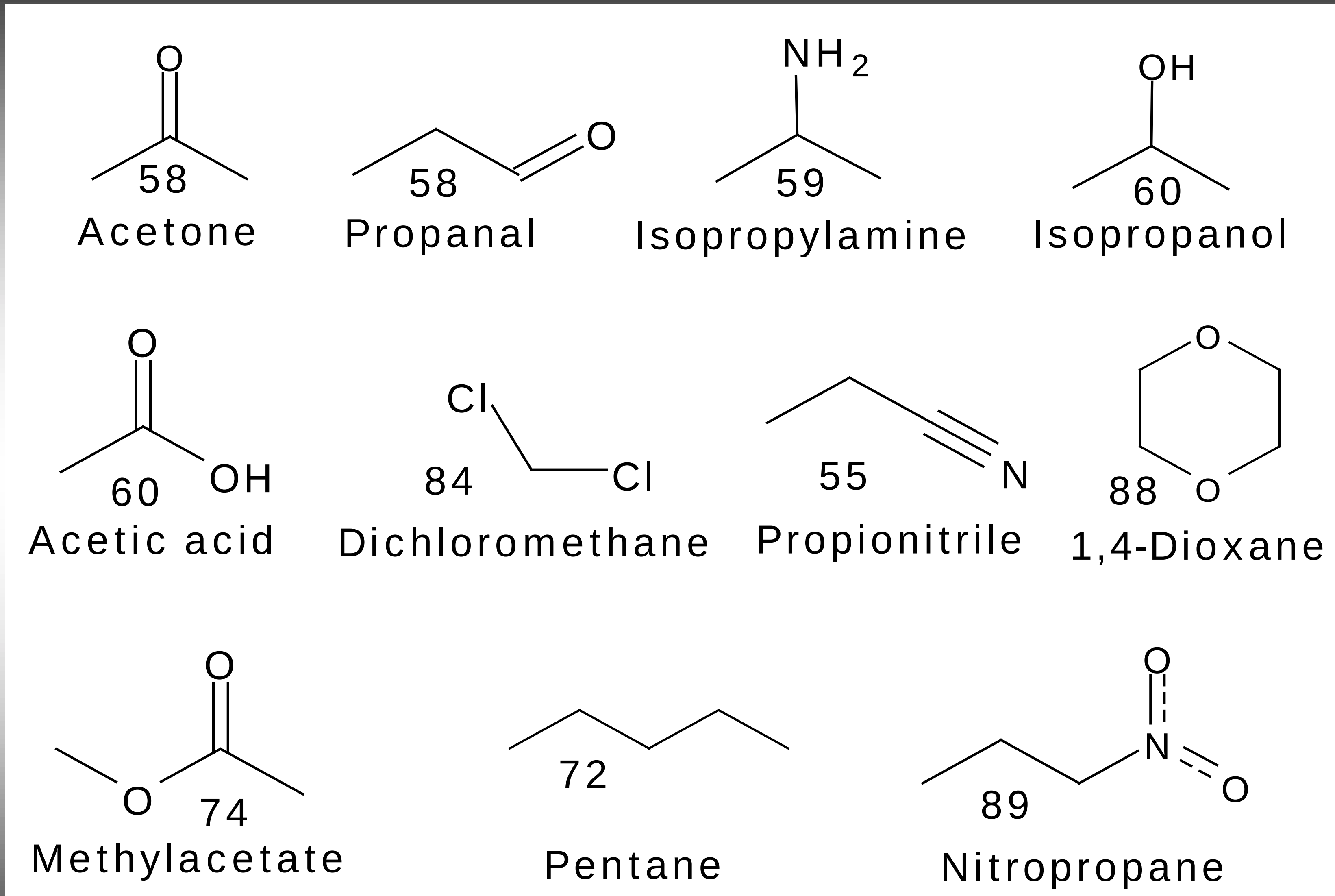
Analytes in Volatile Study



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FID Response Factors for Analytes

Analyte	Response Factor
Acetone	1.78
Isopropanol	1.79
Methylacetate	3.11
Propanal	2.11
Methylene chloride	7.13
Acetic acid	6.41
1,4-Dioxane	2.60
Isopropylamine	1.93
Propionitrile	1.73
Nitropropane	2.15

Analytical Conditions for Evaluation of Fibers with Volatile Analytes

Sample: Water containing 25% NaCl and appropriate 0.05M phosphate buffer, spiked with analytes to a final concentration of 2ppm

Extraction: 15 min with agitation, using Varian 8200 autosampler

Desorption: 2 min, temperature varies, depending on fiber

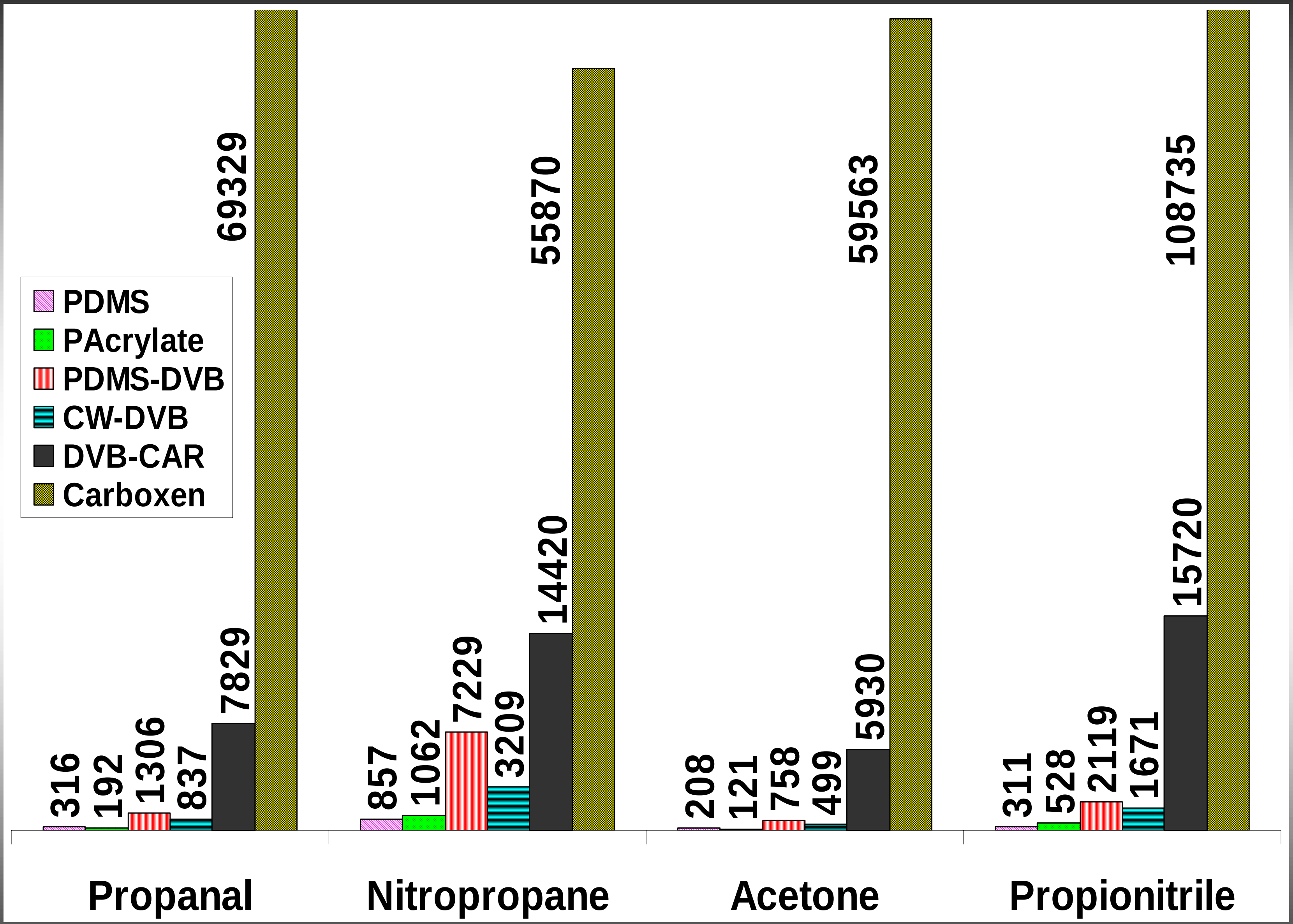
Column: 30m x 0.32mm x 4.0µm SPB™-1 SULFUR

Oven: 40°C (2 min) to 140°C at 8°C/min (1 min)

Inlet: Split/splitless, closed 0.5min, 0.75mm ID liner

Detector: FID

Comparison of Area Responses by Fiber Type



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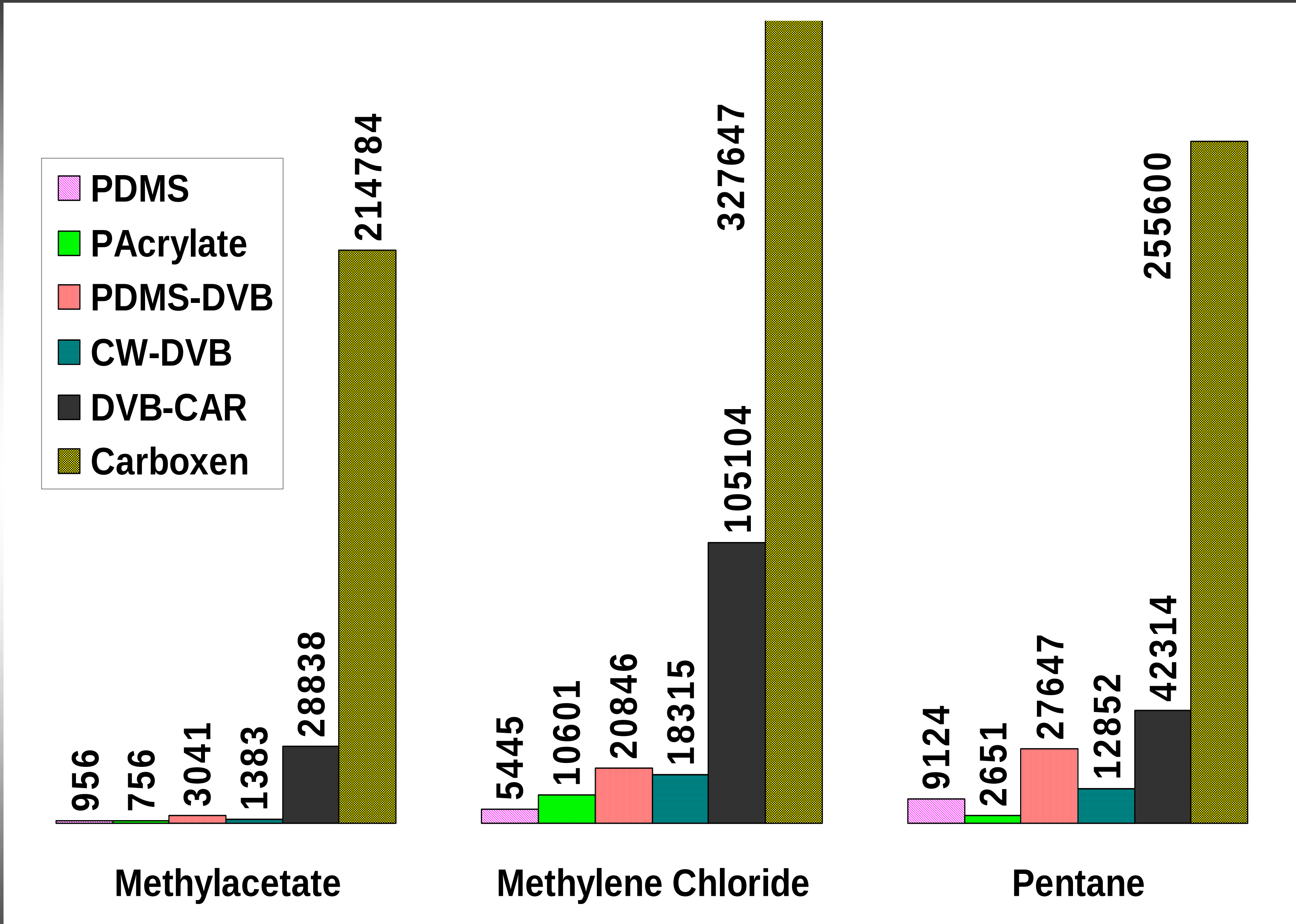
Comparison of Area Responses by Fiber Type



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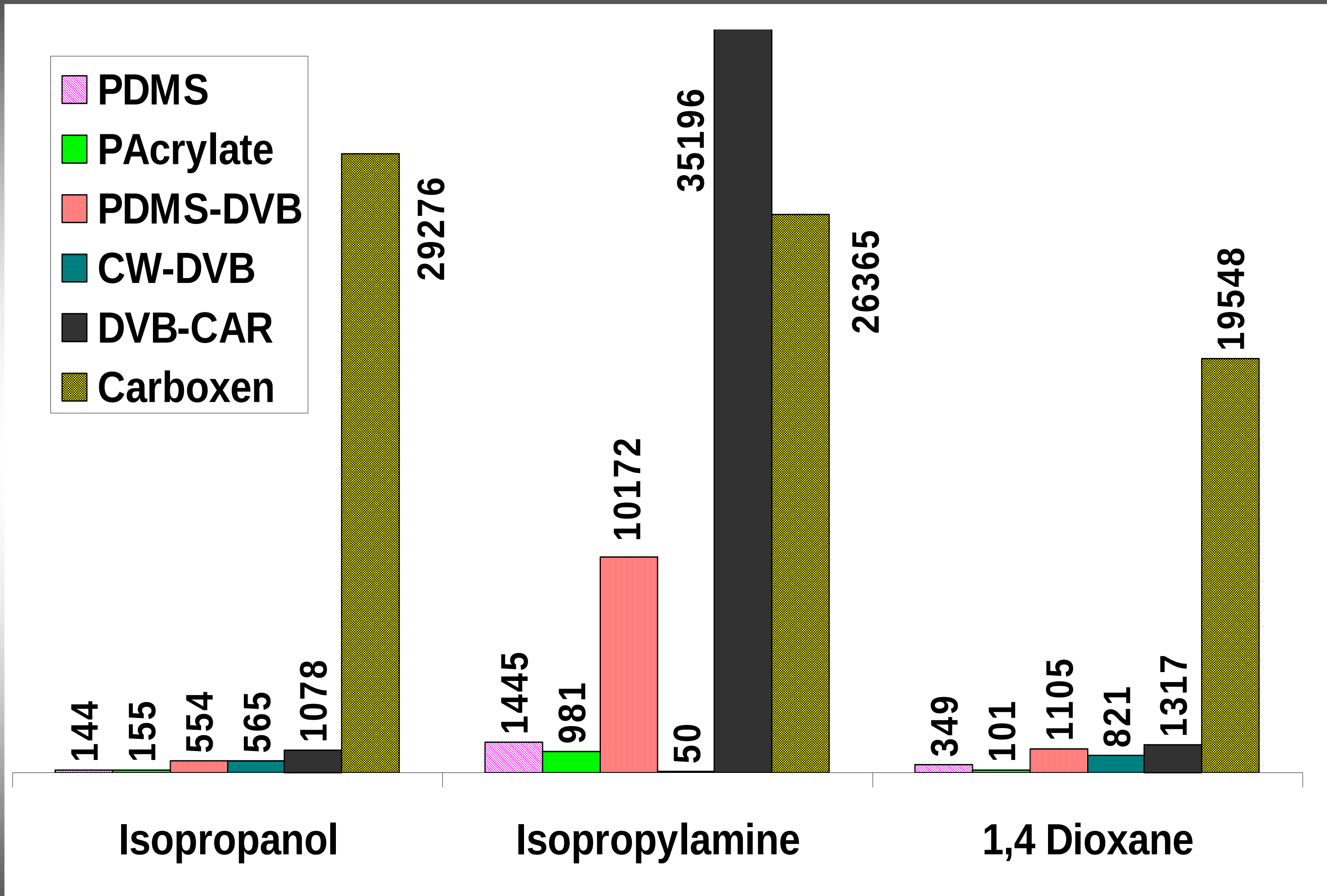
Comparison of Area Responses by Fiber Type



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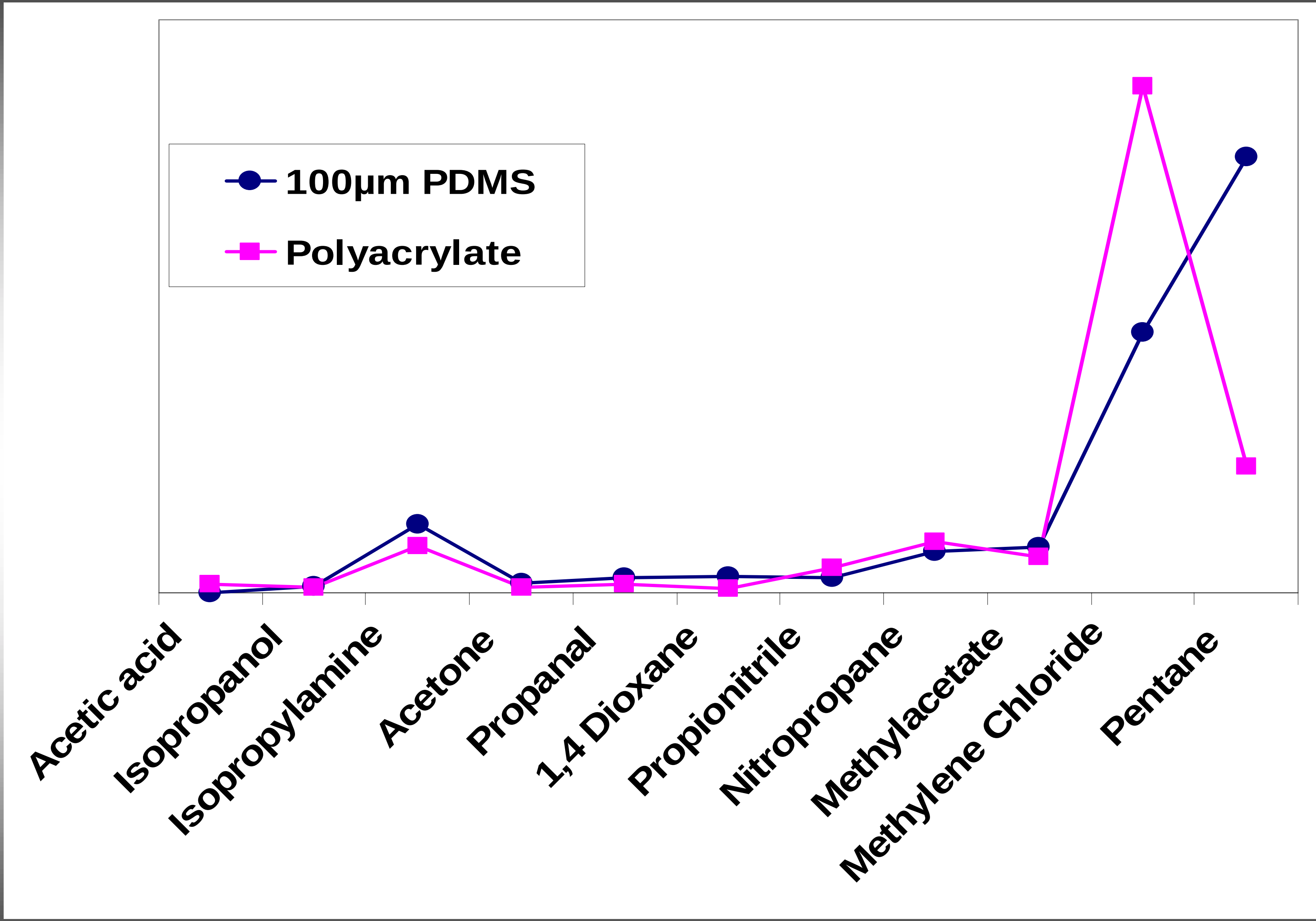
Analyte Polarity vs. Area Response



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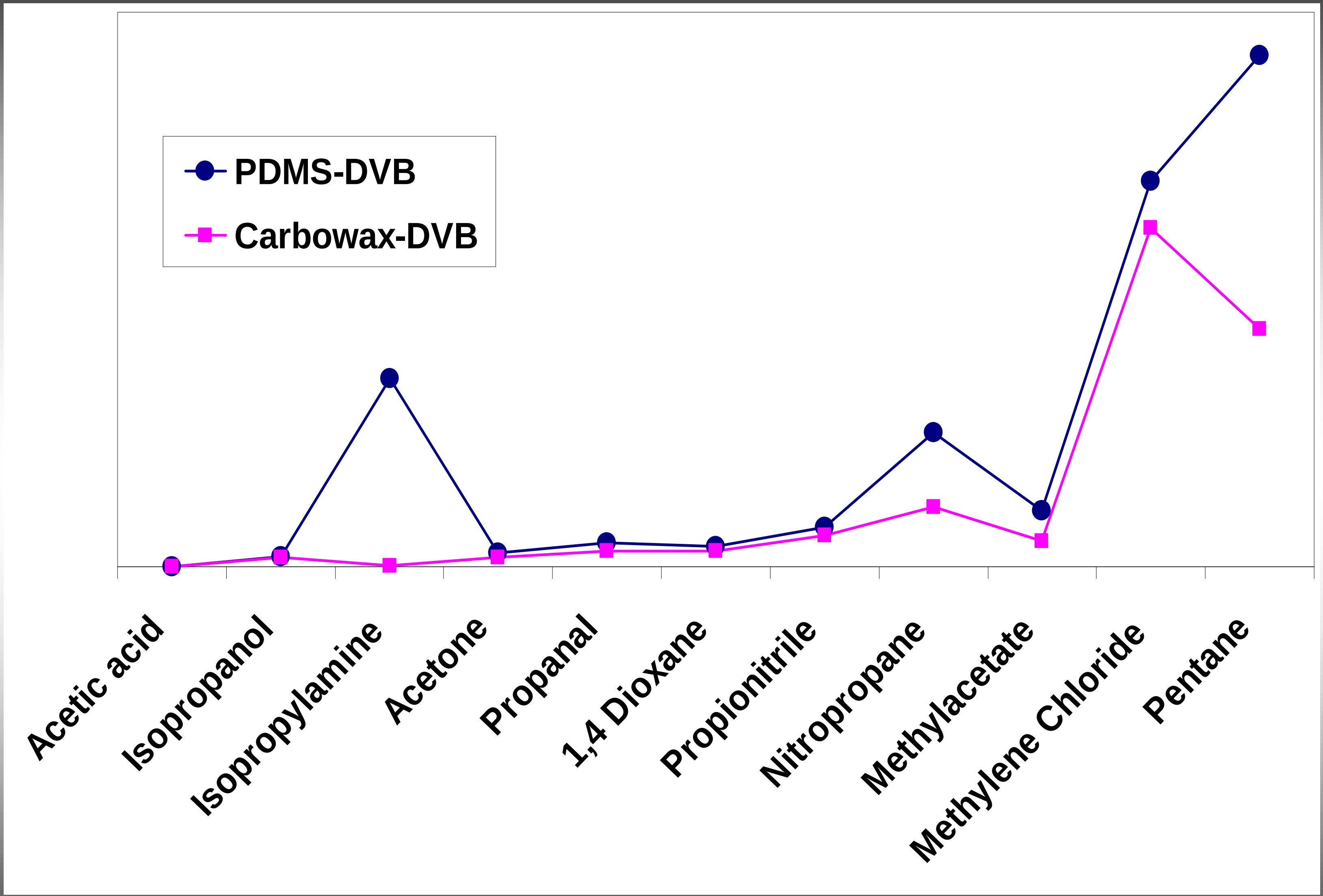
Fiber Polarity vs. Area Response



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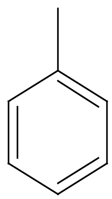
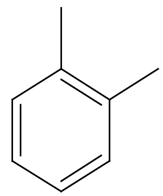
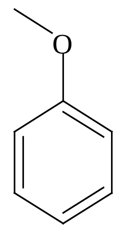
Semi-Volatile Analytes Used in Study



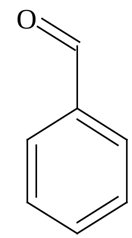
Toluene
92



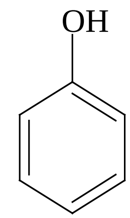
o-Xylene
106



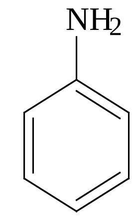
Anisole
108



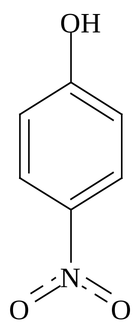
Benzaldehyde
106



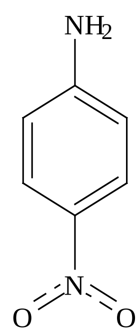
Phenol
94



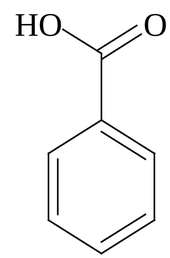
Aniline
93



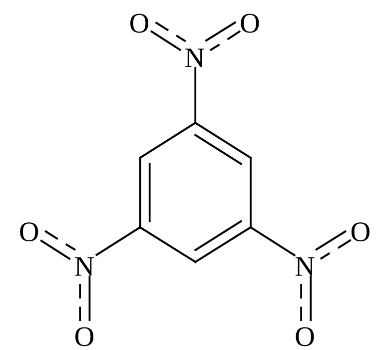
p-Nitrophenol
139



p-Nitroaniline
138



Benzoic acid
122



1,3,5-Trinitrobenzene
213

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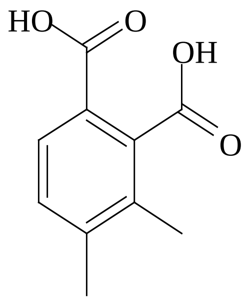
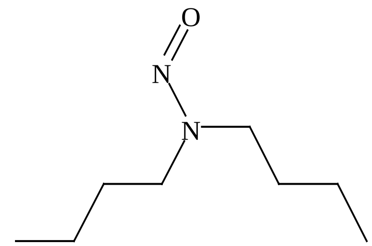
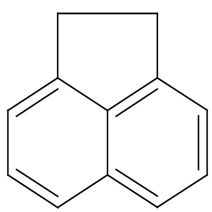
Semi-Volatile Analytes Used in Study (contd.)



Dimethylphthalate
194



N,N-Nitrosodibutylamine
158



Acenaphthene
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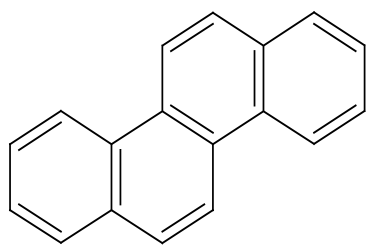
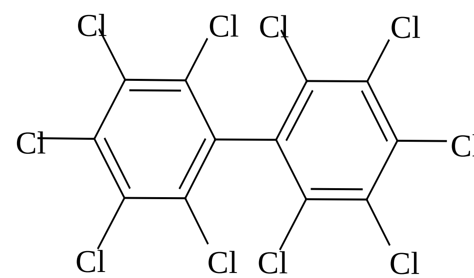


Chrysene
228



Decachlorobiphenyl
499

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Response Factors for Semi-Volatile Compounds in Study

Analyte	Response Factor
Toluene	0.72
o-Xylene	0.83
Anisole	1.13
Benzaldehyde	2.28
Aniline	0.83
Phenol	0.87
Benzoic acid	3.93
n-Dibutylnitrosoamine	2.53
Dimethylphthalate	0.42
Acenaphthene	1.00
p-Nitrophenol	3.87
p-Nitroaniline	3.16
1,3,5-Trinitrobenzene	4.64
Chrysene	0.69
Decachlorobiphenyl	3.16

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Analytical Conditions for Evaluation of Fibers with Semi-Volatile Analytes

Sample:	Water containing 25% NaCl and appropriate 0.05M phosphate buffer, spiked with analytes to a final concentration of 75 ppb
Extraction:	Directly immersed for 30 min with agitation
Desorption:	3 min, temperature varies, depending on fiber
Column:	30m x 0.5mm x 0.25µm PTE™-5
Oven:	45°C (2 min) to 210°C at 10°C/min, then to 320°C at 20°C/min (10 min)
Inlet:	Split/splitless, closed 1 min, 0.75mm ID liner
Detector:	MS ion trap, m/z = 50-515 at 0.6 sec/scan

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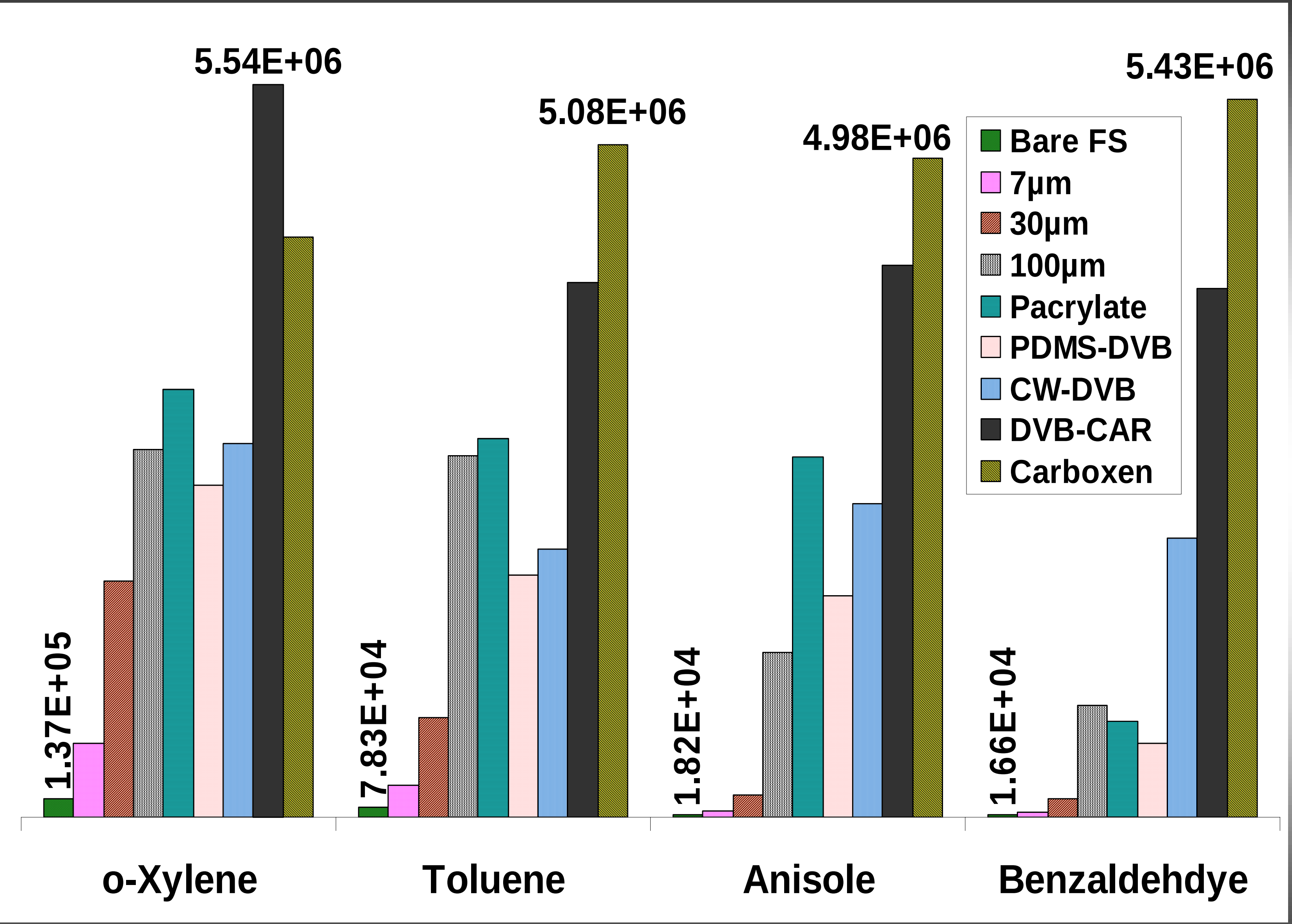
Comparison of Area Responses by Fiber Type



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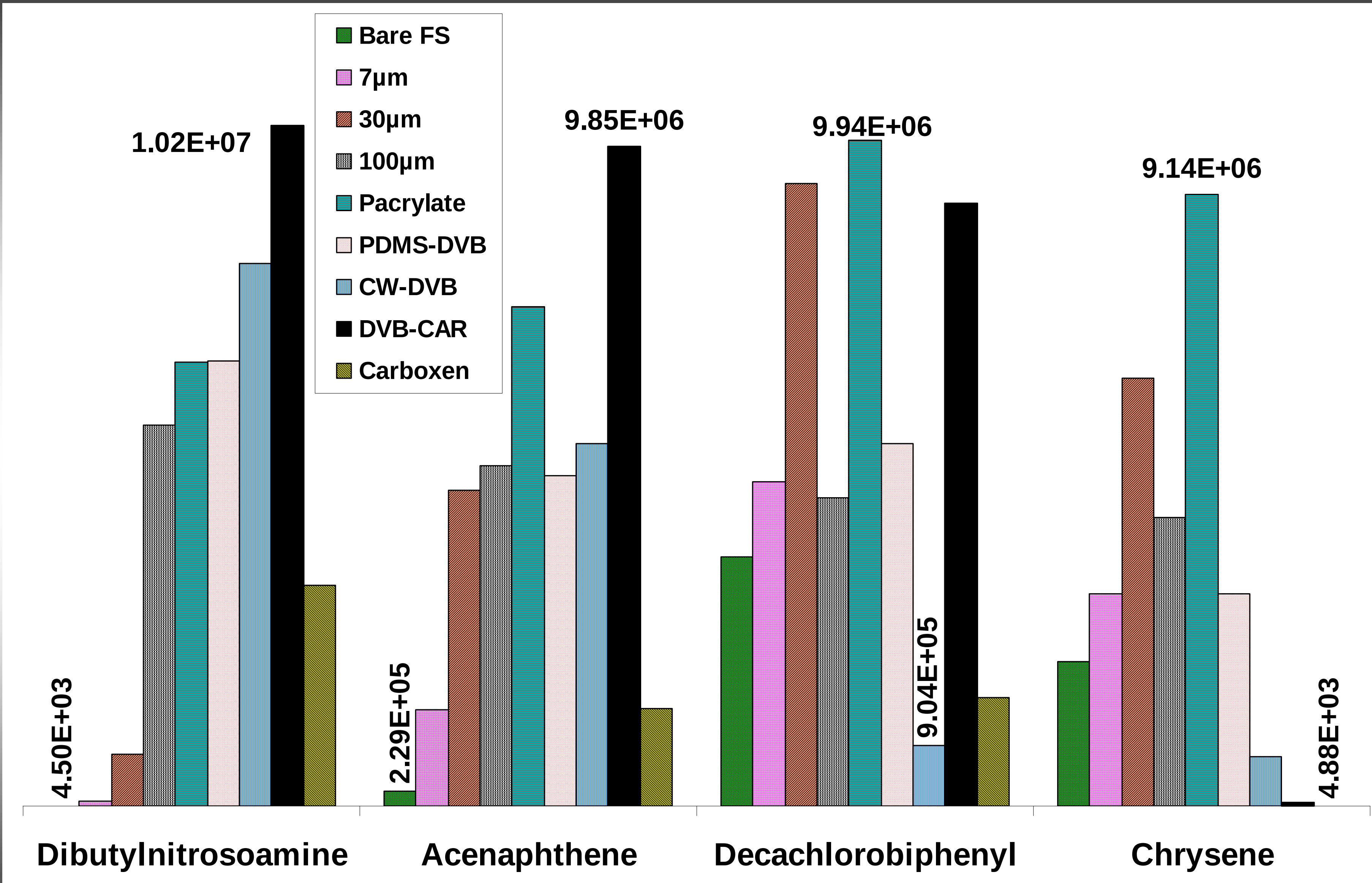
Area Response vs. Fiber Type



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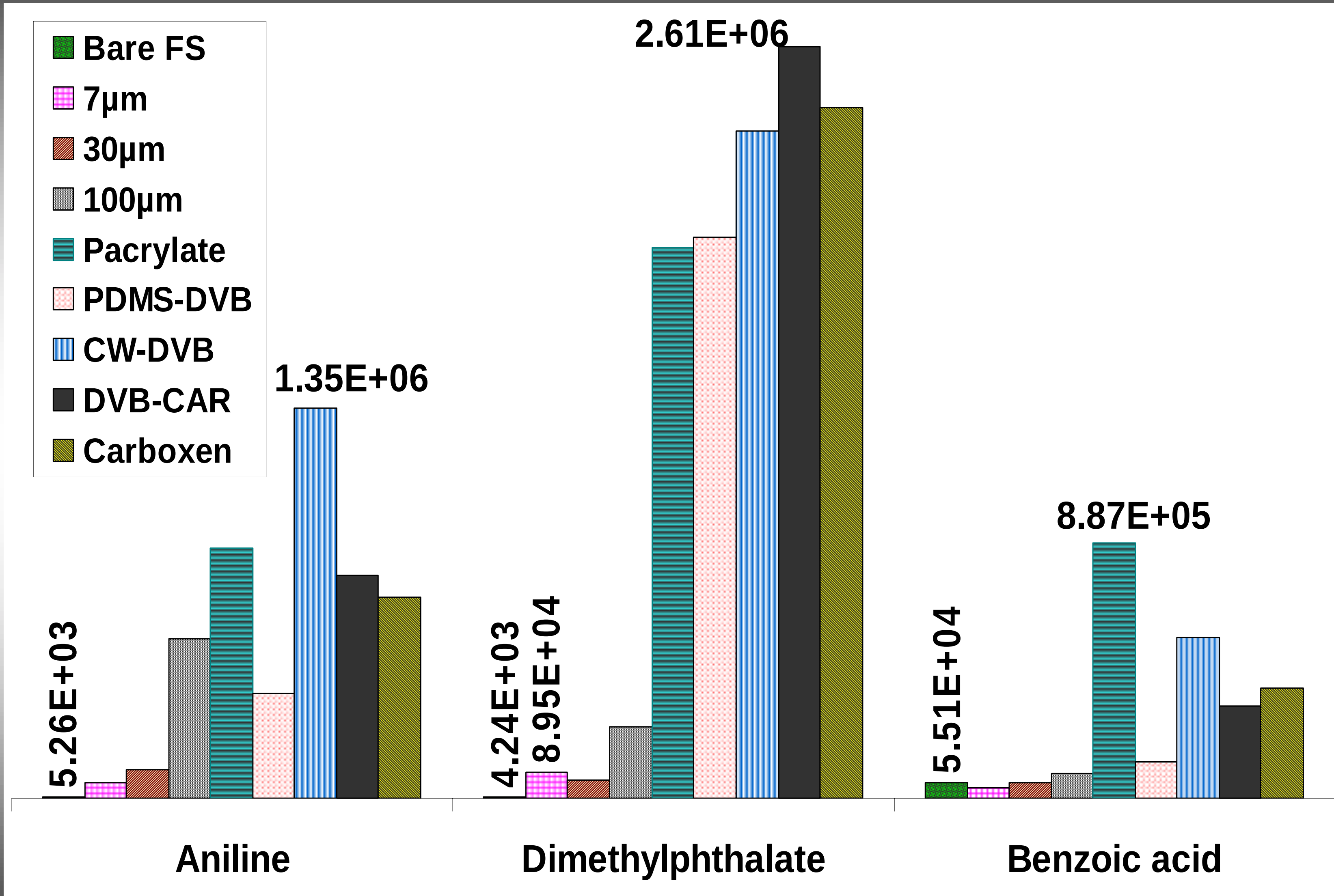
Area Response vs. Fiber Type



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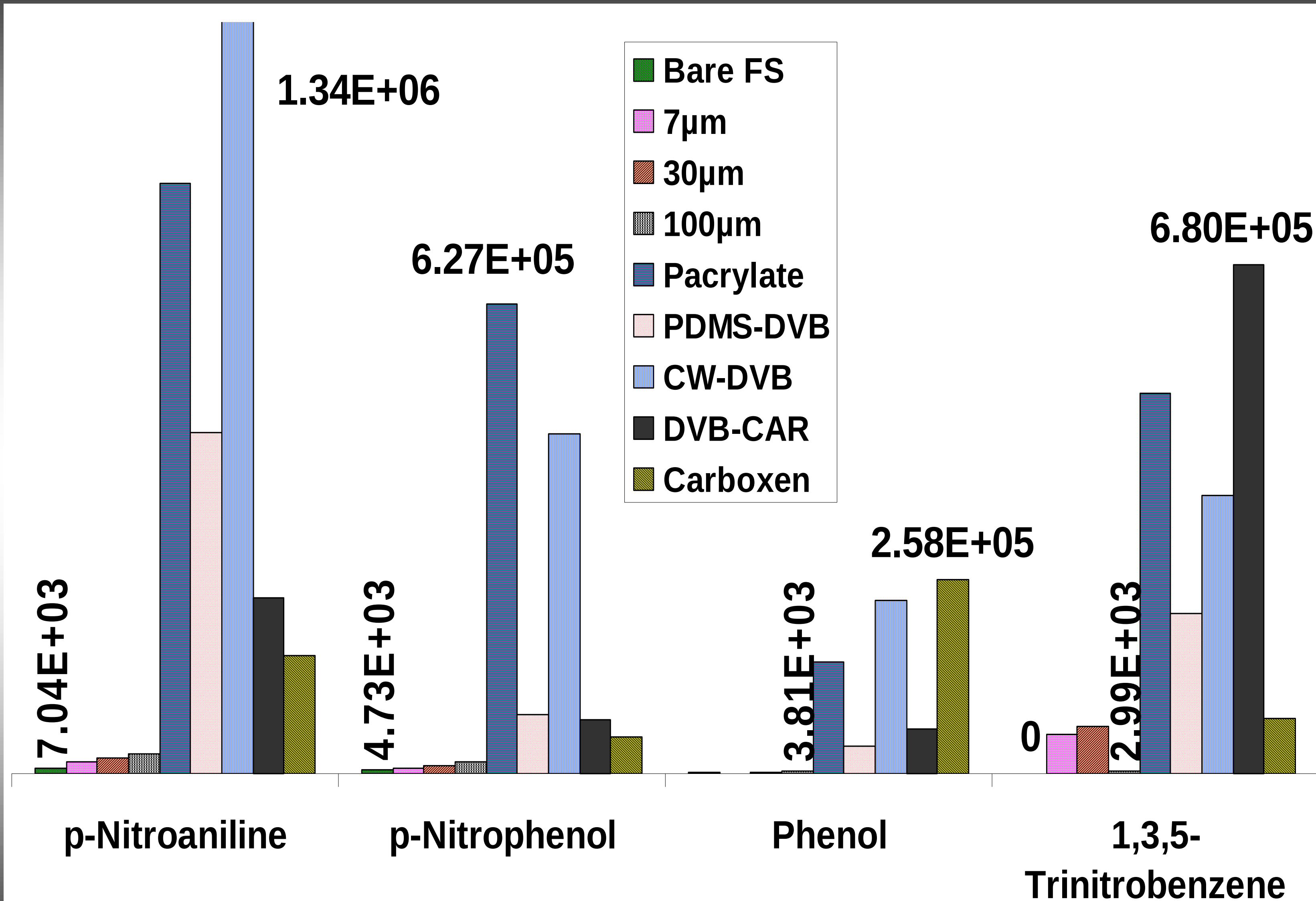
Area Response vs. Fiber Type



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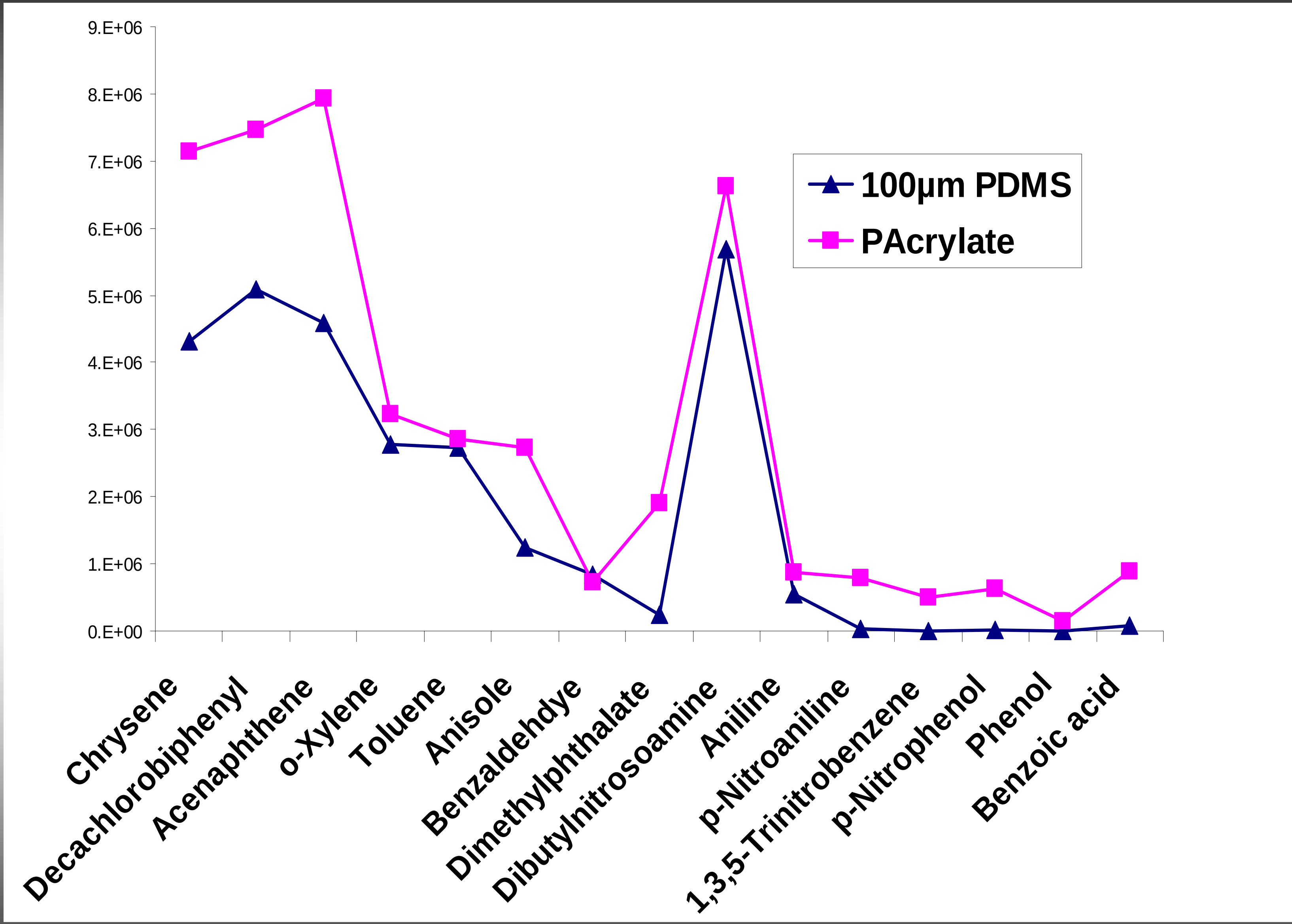
Analyte Polarity vs. Area Response



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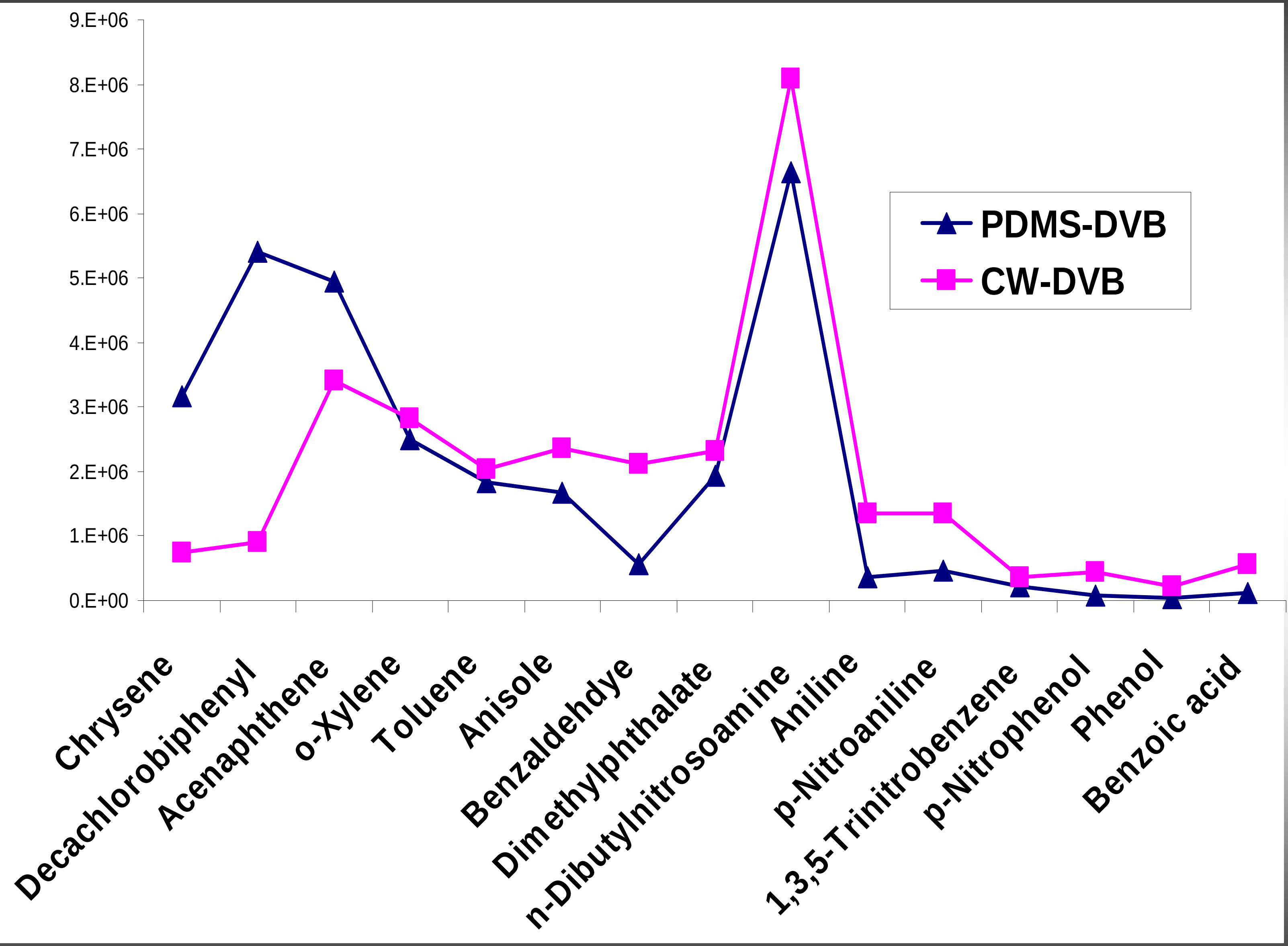
Analyte Polarity vs. Area Response



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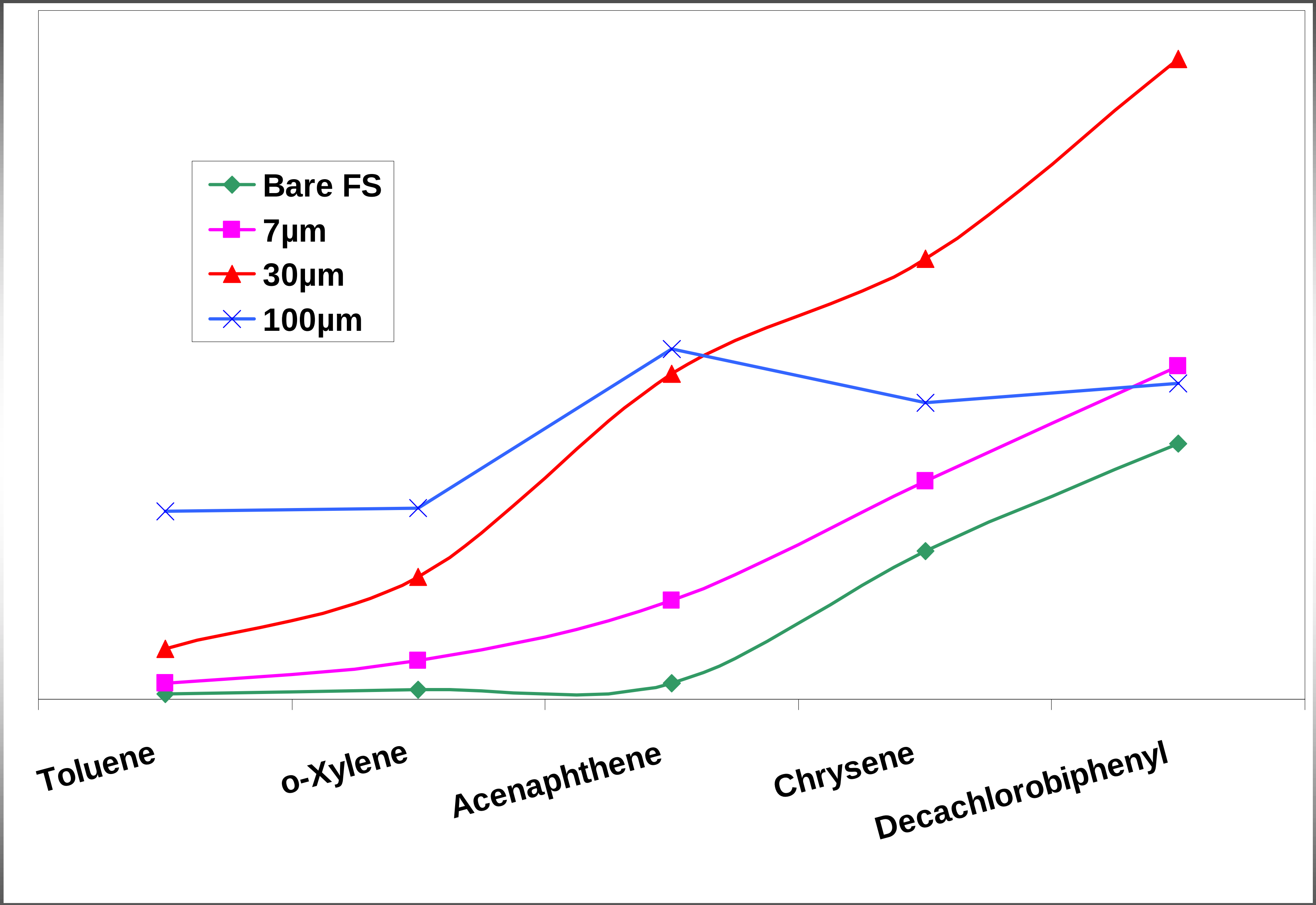
Effects of Coating Thickness on Analyte Recovery



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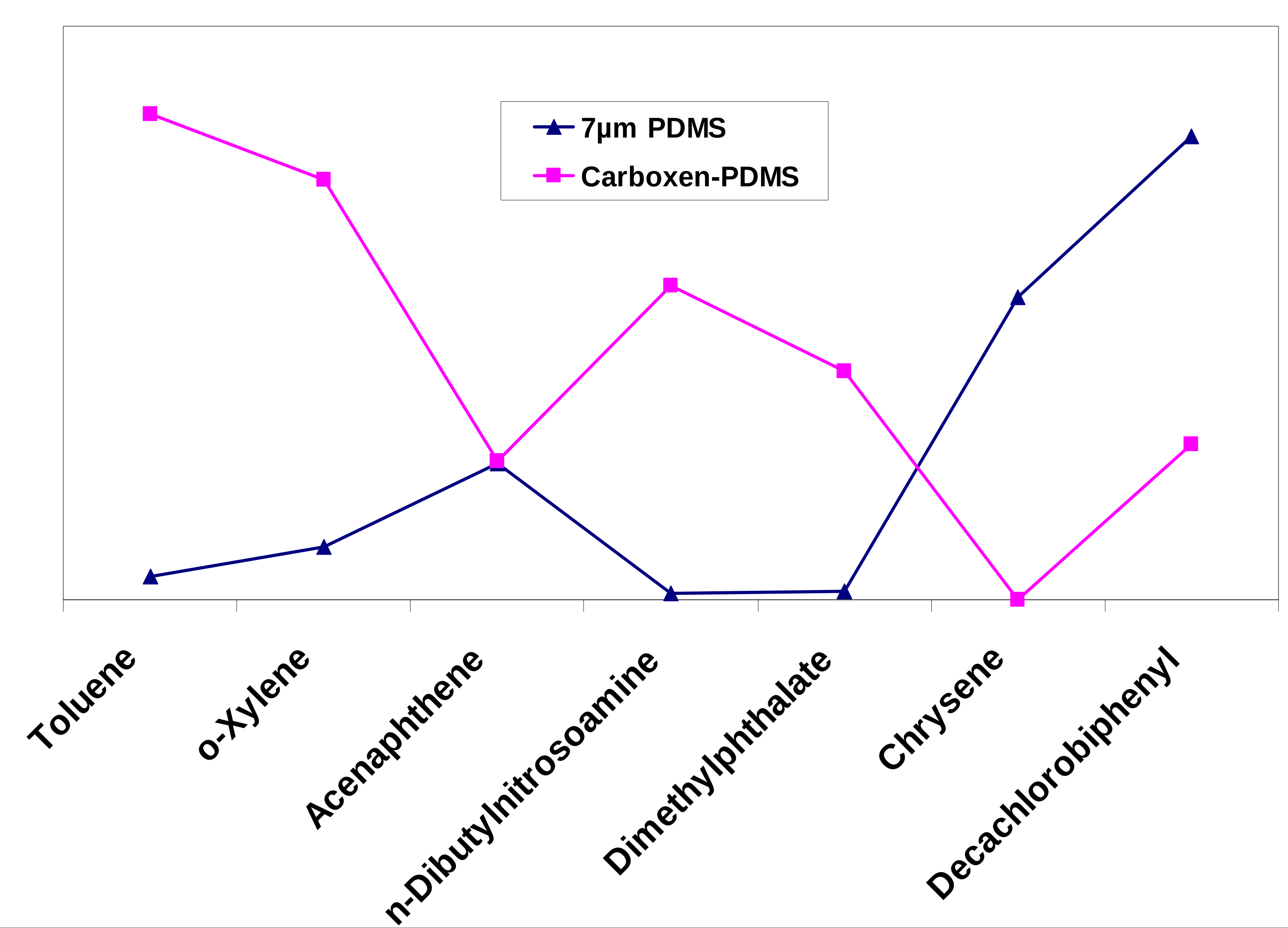
Analyte Size vs. Area Response



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Classical Adsorption Mechanism for a Uniform Surface

$$Ø = \frac{\text{number of adsorption sites filled}}{\text{number of adsorption sites available}}$$

Langmuir's Isotherm

$$Ø = KP_A /(1 + KP_A)$$

where $K = k_a / k_d$ k_a = rate of adsorption k_d = rate of desorption

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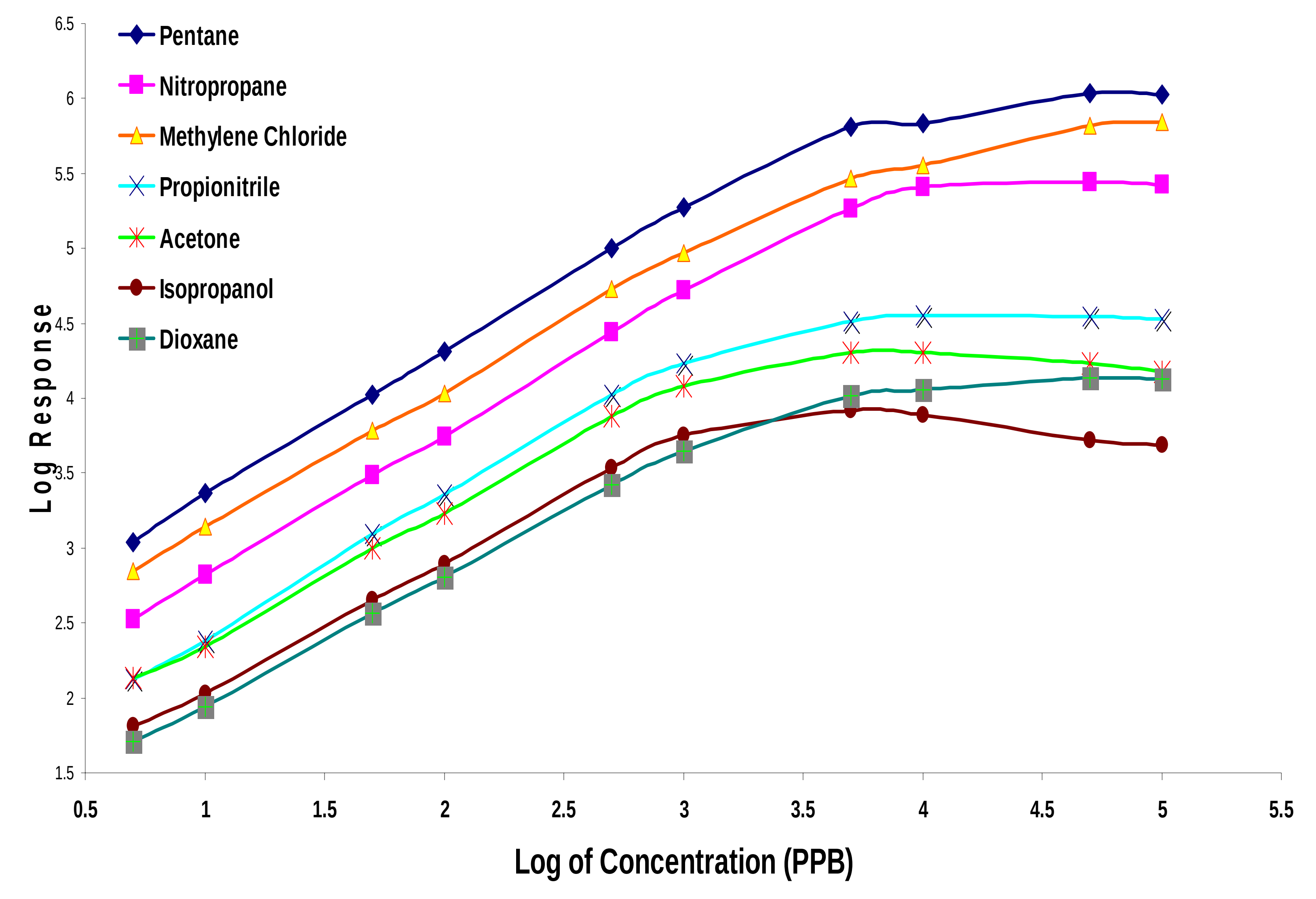
Analyte Response vs. Conc. (Carboxen-PDMS)

15 Min Ext.



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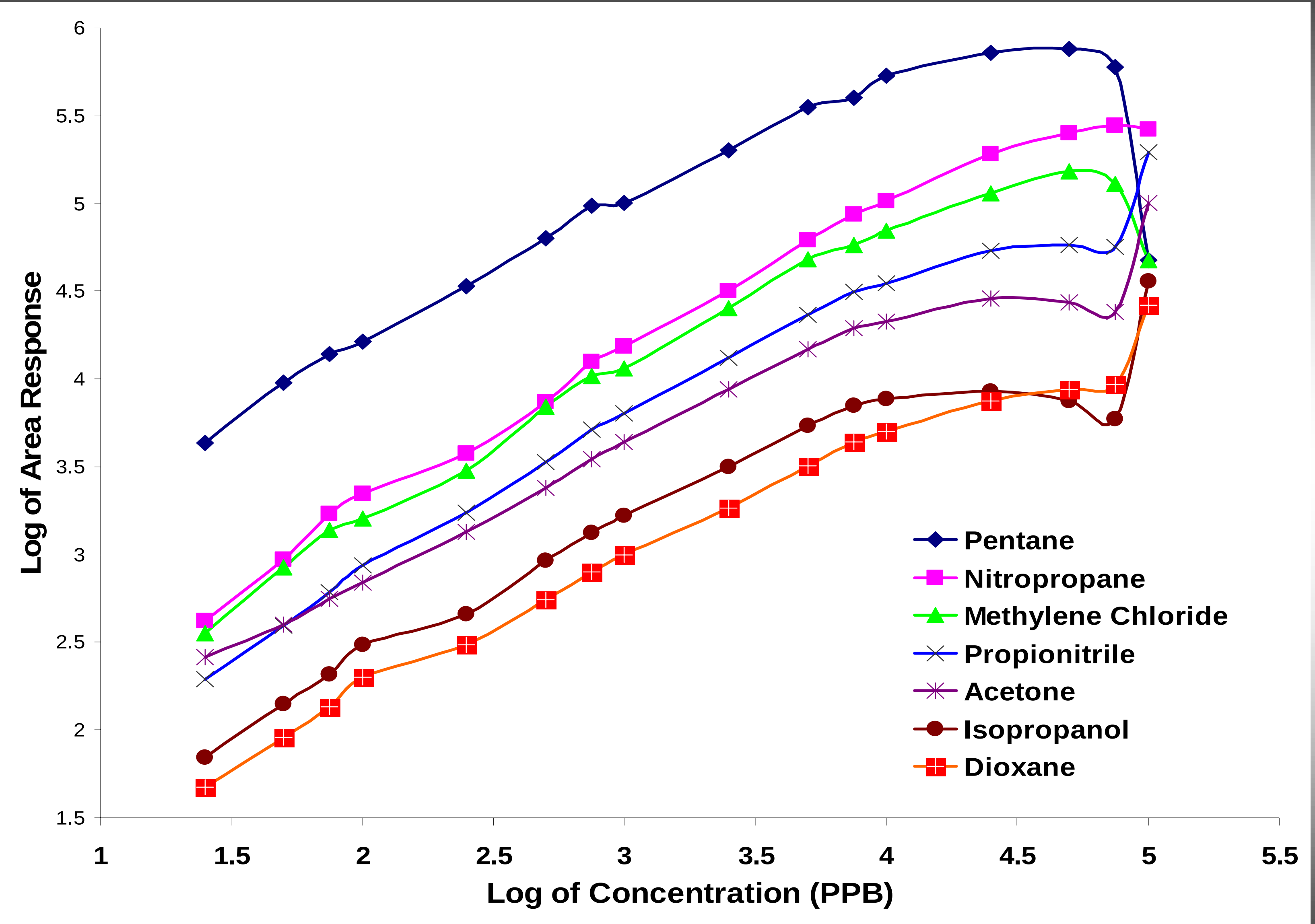
Analyte Response vs. Conc. (Carboxen PDMS 2min Ext.)



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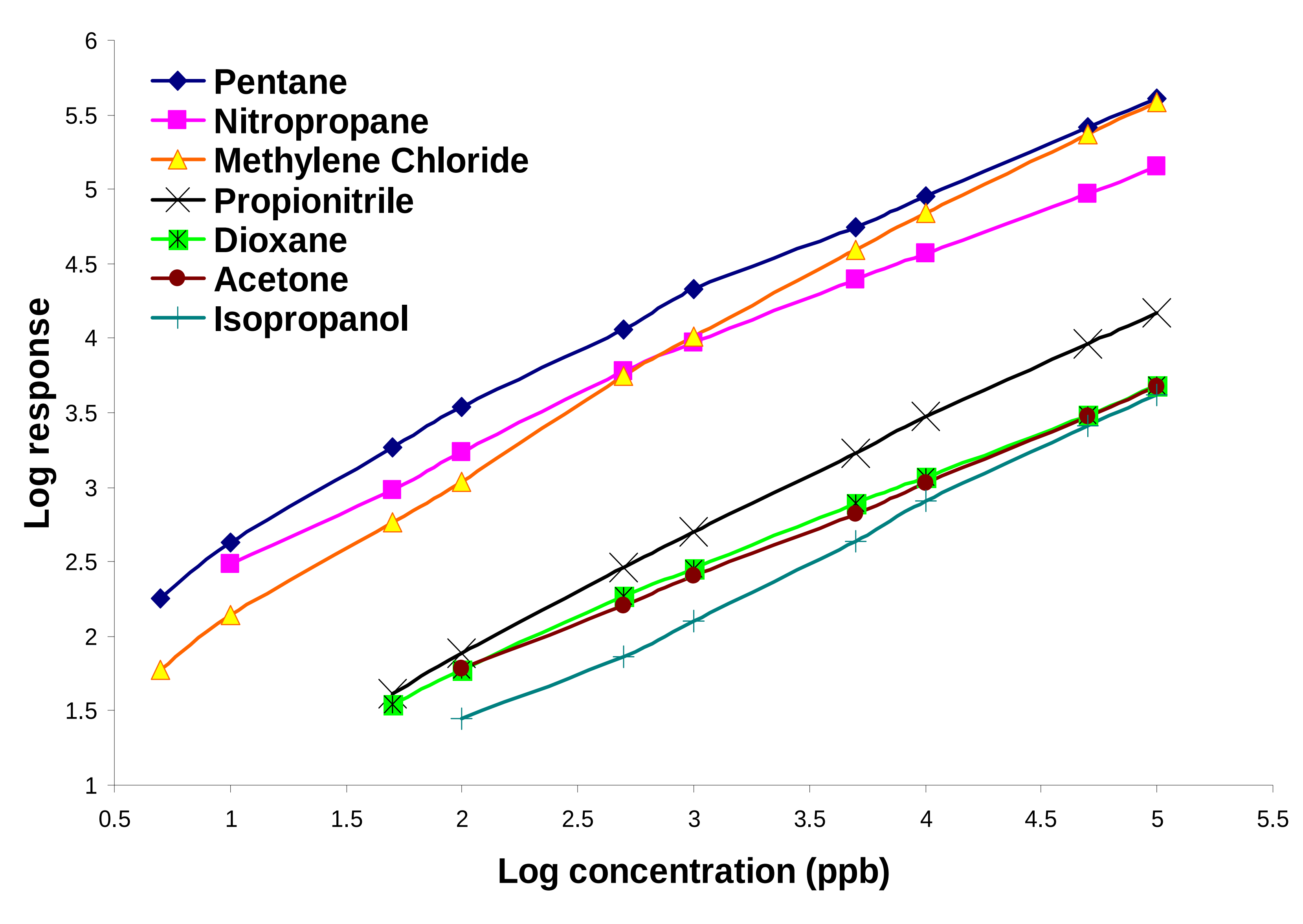
Analyte Response vs. Conc. (PDMS-DVB)



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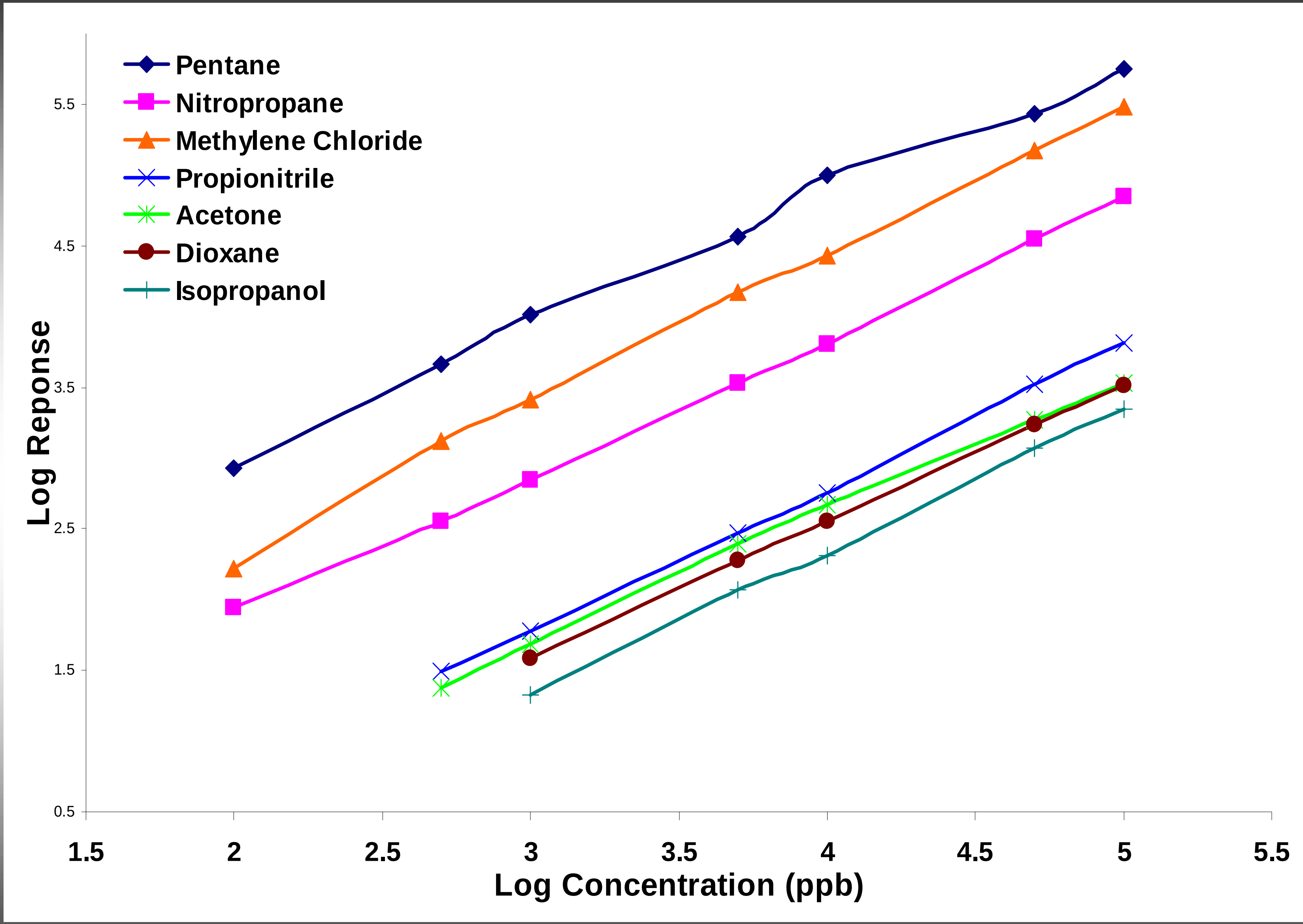
Analyte Response vs. Conc. (100µm PDMS)



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Conclusions

- Carboxen-PDMS is best for extracting small analytes (MW<90).
- For small analytes, analyte polarity has little affect on fibers.
- Analyte polarity affects fiber selection for larger analytes
  - the CW-DVB and Polyacrylate fibers are best or extracting polar analytes
- High MW analytes >150 amu and planar analytes are not extracted well by Carboxen containing fibers.
- Thin absorbent fibers are good for PAHs and PCBs.
- Adsorbent fibers are good for trace level extractions but have limited linear range.
- Absorbent fibers have higher minimum detection but larger linear ranges.

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